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Document Information

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Time required per determination: 30 minutes.

Systematic error: Dependent upon the calibration of the Babcock Sulfonation Flask. (Specified less than ± 1%).

Precision (99% limits): Better than ±1%.

Sample size: 10 ml.

2. Ferrous Sulfamate--Volumetric Determination as Ferrous Iron and Sulfamic Acid.

Application: Aqueous ferrous sulfamate concentration in the range of 10 to 800 g./l. may be determined by this method (e.g., RAS Make-up, Sulfamic Acid Storage).

Description: Ferrous iron and sulfamic acid are determined stepwise. The concentration of ferrous iron is first obtained volumetrically by a potentiometric titration with standard potassium permanganate. The permanganate titration is stopped as soon as the potentiometer indicates that the ferrous ion has all been oxidized. The sulfamic acid concentration of the sample is then determined (after heating the sample to $50^\circ C$.) by titrating with standard sodium nitrate until the sulfamate ion has been converted to sulfate. Since ferric iron subdues the potentiometric end-point of the permanganate titration and completely obscures the nitrite end point, it must be complexed as it is formed by the addition of phosphoric acid to the sample prior to titration.

Time required per determination: 60 minutes (30 minutes for ferrous iron, and an additional 30 minutes for sulfamate).

Systematic error: Ferrous iron--Approximately minus 10%.
            Sulfamic acid--Approximately minus 3%.

Precision (99% limits: Ferrous iron--Better than ±4%.
            Sulfamic acid--Better than ±6%.

Sample size: Sample should contain from 5 to 10 milligrams of ferrous sulfamate (e.g., approximately 0.5 ml. of RAS).

3. Hydrogen Ion by Fluoride Complexing

Application: The hydrogen ion concentration of aqueous and organic solutions (greater than 0.1 g./l.) may be obtained by this method. Since the determination has proven satisfactory for small sample volumes, it has been selected for use on radioactive solutions such as RAW. This method, rather than the potassium oxalate method, rather than the potassium oxalate method, is used for solutions containing ferric iron, since fluoride forms a "tighter" iron complex than the iron-oxalate complex. The uranium and iron interferences are minimized by the formation of fluoride complexes when potassium fluoride is added to the sample. Since chromate is not complexed, its concentration must be known so that a suitable correction may be made.

Description: The hydrogen ion concentration is determined volumetrically by a potentiometric titration with sodium hydroxide to an inflection point in the region of pH 8 to 9. Potassium fluoride is added to the sample solution prior to titration to complex iron and uranium which would interfere with the determination.

Time required per determination: 45 minutes.

Systematic error: Approximately zero to minus 2% (estimated).

Precision (99% limits): Approximately ± 1 g./l.

Sample size: Method is scaled down for micro determinations. Samples as small as 0.010 ml. may be used.

4. Hydrogen Ion by Oxalate Complexing

Application: The hydrogen ion concentration of both aqueous and organic solutions (greater than 0.1 g./l.) may be determined by this method. Since the determination requires small sample volumes, it may be used on radioactive solutions. Uranium interferes with the method and is complexed by adding potassium oxalate. For solutions such as RAF and RAW containing appreciable phosphate ion concentrations, the phosphate ion must be known and a suitable correction made since the hydrogen which is present as $HPO_4^=$ is not titrated.

Description: The hydrogen ion concentration is determined by a potentiometric titration with standard sodium hydroxide to an inflection point in the range of pH 6 to 7. If uranium is present in the sample, potassium oxalate is added to minimize interference. Water is added to organic samples and the potentiometric titration is made on the aqueous phase containing the extracted hydrogen ion.

Time required per determination: Samples containing no interfering ions -- 30 min.
Samples containing interfering ions -- 45 min.

Systematic error: Approximately zero to minus 2%.

Precision (99% limits): Approximately ± 1 g./l. (For samples requiring approx. 0.005 mole NaOH for neutralization.)

Sample size: If the radioactivity of the sample permits, sufficient sample should be taken to require approximately 0.005 mole of sodium hydroxide for neutralization. Samples as small as 0.1 ml. may be used with some (as yet not exactly known) reduction in the precision.

5. Total Nitrate Ion

Application: The total nitrate ion concentration of all aqueous Uranium Recovery Plant solutions may be determined by this method. The result obtained is occasionally used to determine the total hydrogen ion

(associated and dissociated) concentration by difference when the concentrations of the other ions (uranium, sodium, phosphate, and sulfate) are known.

Description: An excess of sulfuric acid (approximately 6 N) is added to the sample and the more volatile nitric acid formed is distilled under vacuum (at 0.5 mm. mercury in a boiling water bath) and collected in a coil immersed in a dry-ice slush. The condensate is melted, diluted with water, and titrated with standard base to the methyl red end point.

Time required per determination: 30 minutes.

Systematic error: Approximately minus 1%.

Precision (99% limits): For solutions containing approximately 3 to 6 M NO_3^- better than $\pm$ 2%. (It is expected that with increased experience with the method the precision may be improved to better than $\pm$ 0.5%.)

Sample size: 0.010 to 0.050 ml.

6. pH Measurement by One-Drop Electrode

Application: The hydrogen ion concentration of small amounts of radioactive aqueous solutions may be determined by the one-drop electrode. From the determination, the completeness of neutralization of wastes to be stored in underground tanks may be determined.

Description: The pH is determined potentiometrically by placing about one drop of sample into the cup-shaped, one-drop electrode of a Model G Beckmann pH meter.

Time required per determination: 15 minutes.

Systematic error: Dependent upon standards used to calibrate pH meter.

Precision (99% limits): $\pm$ 0.05 pH units.

Sample size: One drop (not less than 0.075 ml.).

7. Phosphate--Volumetric Method

Application: Since this method requires a small sample volume it is suitable for determining the phosphate concentrations of highly radioactive Uranium Recovery Plant solutions such as RAF and RAW containing from 2 to 50 g. phosphate/l.

Description: Phosphate ion is precipitated as ammonium phospho-molybdate from an ammonium nitrate-nitric acid solution. The filtered and washed precipitate is dissolved in a measured excess of standard sodium hydroxide. The excess sodium hydroxide is titrated with standard hydrochloric acid to a phenolphthalein end point.

<u>Time required per determination</u>: 30 minutes.

<u>Systematic error</u>: Dependent upon accuracy of standard solution make-up. Probably less than 0.1 g./l.

<u>Precision (99% limits)</u>: Estimated to be between + 0.4 and -0.4 g./l.

<u>Sample size</u>: The sample chosen should contain approximately 0.5 to 1.0 milligram of phosphate.

8. Sodium Determined by the Flame Spectrophotometer

<u>Application</u>: Aqueous phase sodium concentrations greater than 0.01 g./l. may be determined by this method. The concentration of the solution must be fairly well established (except Na concentration) for the result obtained with the sample is compared with standard solutions of approximately the same overall composition.

<u>Description</u>: An aqueous solution of sodium salt is atomized and then introduced at a carefully controlled rate into a flame where it is ignited giving off the characteristic yellow sodium color. The intensity of light emission at a wavelength of 584 millimicrons is measured with a spectrophotometer and compared with standard sodium solutions measured in the same manner.

<u>Time required per determination</u>: 15 minutes.

<u>Systematic error</u>: Approximately plus 1%.

<u>Precision (99% limits)</u>: Approximately ± 10%.

<u>Sample size</u>: A sample should contain approximately 0.0005 grams of sodium.

9. Spectrographic Assay of Uranium

<u>Application</u>: The concentrations of trace impurities in concentrated uranium solutions (i.e,, RCU, or Concentrated UNH solution) or in UO_3 may be determined by this method.

Concentrations of impurities in U_3O_8 as low as the following may be detected:

Ag	0.1 p.p.m.	Co	100 p.p.m.	Mg	10 p.p.m.	P	5 p.p.m.
As	5	Cr	10	Mn	5	Pb	5
B	0.2	Cu	20	Mo	20	Sb	2
Be	0.1	K	50	Na	5	Sn	5
Bi	1	Li	5	Ni	10	Zn	100
Cd	1						

<u>Description</u>: The sample is evaporated to dryness, then heated to 700 to 800°C. in the presence of air to convert UNH (or UO_3) to U_3O_8. An

aliquot of the U_3O_8 and a small amount of pure gallium oxide (two weight per cent) are placed in a graphite crater electrode and arced using a direct-current source. The spectrum of the gases volatilized by the arc is photographed using a quartz prism spectograph and the concentrations of impurities are estimated by visual comparison of the spectrum with the spectrum of previously prepared standards. The gallium oxide volatilizes during arcing "flushing" volatile impurities from the U_3O_8 sample.

Time required per determination: Elapsed time -- 8 hours.
                                   Operator time -- 2 hours.

Systematic error: Dependent upon accuracy of the standards and the sensitivity of the photographic plates. Generally the systematic error is less than the lowest detectable concentration.

Precision (99% limits): At the lower limits indicated above precision of approximately ± 100% may be obtained. At higher concentrations precisions of + 100% and minus 50% may be attained.

Sample size: For a single spectorgraphic "shot" (a determination on approximately one-third of the spectrum) a minimum of 100 milligrams of U_3O_8 is needed. For a total analysis, duplicate determinations over the entire spectrum, a minimum of 600 milligrams of U_3O_8 is required.

10. Sulfate Ion -- Volumetric Determination

Application: Since such a small amount of sulfate is required, this method is used for the determination of the sulfate concentration of the highly radioactive aqueous feed (RAF) and aqueous waste solutions (RAW).

Description: Sulfate present in the sample is reduced by a mixture of reducing acids (HI and hypophosphorous acids) and the hydrogen sulfide gas formed from the sample solution (swept by a stream of pure nitrogen) is absorbed in an ammoniacal cadmium chloride solution. The solution containing the cadmium sulfide is acidified with hydrochloric acid and the sulfide is oxidized to sulfur by the addition of a measured excess of standard iodine (0.1 N iodine in KI). The iodine excess is titrated with standard thiosulfate using starch indicator.

Since nitrates interfere with the method they are initially removed as nitrogen or volatile nitrogen oxides by adding formic acid and boiling.

Time required per determination: 30 minutes.

Systematic error: Approximately minus 2%.

Precision (99% limits): Better than ± 2%.

Sample size: The sample chosen should contain approximately one to five milligrams of sulfate ion.

## 11. Tributyl Phosphate -- Hydrolysis Method

Application: The concentration of tributyl phosphate (plus DBP) soluble in slightly radioactive aqueous solutions (e.g., RCU, ROW) may be determined by this method. Dibutyl phosphate, if present in the aqueous phase, is analyzed TBP.

Description: TBP is quantitatively extracted from the sample solution with carbon tetrachloride. A small amount of concentrated sulfuric acid is added to the separated carbon tetrachloride. The CCl_4 is rapidly boiled off, leaving phosphoric acid (formed by the hydrolysis of TBP) in the aqueous residue. Next nitric acid and ammonium persulfate are added and the solution is heated to boiling to destroy any organic residue. Phosphate is precipitated from the solution as ammonium phospho-molybdate upon the addition of ammonium nitrate and molybdate-citrate reagent. The solution is filtered and the precipitate is washed with neutral KNO_3 solution. The precipitate is dissolved (see equation below) with a measured volume of standard NaOH and the excess NaOH is back-titrated with standard HCl to a phenolphthalein end point.
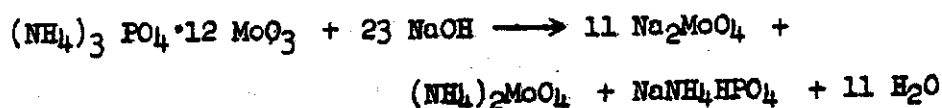
$$(NH_4)_3 PO_4 \cdot 12 MoO_3 + 23 NaOH \longrightarrow 11 Na_2MoO_4 +$$

$$(NH_4)_2MoO_4 + NaNH_4HPO_4 + 11 H_2O$$

Time required per determination: 45 minutes.

Systematic error: Approximately plus 1%.

Precision (99% limits): ± 3 to 4%.

Sample size: Dependent upon the TBP concentration in the sample. Sample sizes should be chosen, if possible, so that the sample contains approximately 5 to 10 milligrams of TBP. For an RCU sample containing approximately 0.2 g.TBP/l., 25 ml. of sample is required. Since the TBP concentration in RAW is expected to be less than 0.01 g.TBP/l. the method is not applicable for the RAW.

12. Tributyl Phosphate -- Infrared Method

Application: Concentrations of tributyl phosphate in uranium recovery process solvent above 4% by volume may be determined by this method. The method may be used to detect variations in the tributyl phosphate concentrations of the solvent recycled in the plant. Concentrations of UNH up to 5 g./l. which may be present in RCU do not appreciably affect the method. Nitric acid corrodes the sample-cell windows and must be removed before analysis by the addition of an excess of anhydrous potassium carbonate. The interference of monobutyl and dibutyl phosphates is minimized by an initial potassium carbonate treatment.

Description: After removing interfering impurities from the sample with potassium carbonate the clear sample is placed in a cell and a fixed wave-length infrared light (approximately 1031 waves/per cm. or 9.70 microns) is passed through a known depth of sample. The absorption

of the sample -- measured by an infrared spectometer -- is compared with the absorption of standard solutions.

Time required per determination: 20 minutes.

Systematic error: Dependent upon accuracy of standard solutions used in making calibration curves and the frequency of checking of instrument "drift" with standard samples. Over extended operating periods the spectrophotometer may drift as much as 3 volume per cent TBP. With frequent checking the systematic error may be maintained as low as plus or minus 0.1% TBP.

Precision (99% limits): Better than ± 0.3% TBP.

Sample size: 5 ml. (Volumes as small as 2 ml. may be used if necessary).

13. Uranium by Chromous Sulfate Titration

Application: The method may be used for organic or aqueous phase samples containing more than one gram of UNH per liter (e.g., RAF, 241-WR Vault). Nitrates interfere with the method and must be removed by heating with sulfuric and formic acids. If iron and phosphate are both present in a sample the method should not be used. However, the method may be used if either iron or phosphate is present alone.

Description: Uranium is determined volumetrically by titrating to the potentiometric end point with standardized chromous sulfate solution.

Time required per determination: 15 minutes.

Systematic error: Approximately minus 0.5%.

Precision (99% limits): Approximately ± 3%.

Sample size: The sample size is dependent upon the UNH concentration. Sample sizes should, if possible, be chosen so that the sample contains from 7 to 15 milligrams of UNH. (Approximately 0.1 ml. of HW No. 4 Flowsheet RAF solution.)

14. Uranium by Coulometric Titration

Application: This method may be used for the determination of uranium concentrations as low as 1 g./l. in aqueous samples.

Description: The sample and added iron solution are passed through a lead reductor column to reduce the uranium and iron to the quadrivalent and bivalent states, respectively. The solution is then placed in a coulometer cell and a constant current is passed through the solution until the potentiometer "break" is reached. This break represents the conversion of all the uranium in the solution to U(VI). The length of time the current flows before the break occurs is dependent upon the

uranium concentration of the sample. Nitrate ion interferes with the method and must first be removed by boiling the sample in the presence of hydrobromic acid.

Time required per determination: Approximately 45 minutes.

Systematic error: Approximately plus 1%.

Precision (99% limits): Better than ± 5%.

Sample size: The sample chosen should contain approximately one to ten milligrams of uranium (approximately 0.01 to 0.1 ml. of HW No. 4 Flow-sheet RAF solution).

15. Uranium by the Fluorophotometer

Application: The fluorophotometer (also called "fluorimeter") may be used to detect low uranium concentrations, from 0.0001 to 1 g.UNH/l., in both aqueous and organic samples.

Description: Uranium compounds, when fused with sodium fluoride, fluoresce when exposed to ultraviolet light, the intensity of fluorescense being proportional to the amount of uranium present. A mono-chromatic ultraviolet light (365 millimicrons) is directed on a care-fully prepared fused sample. The fluorescent light is filtered, and the intensity of the monochromatic fluorescent light (555 millimicrons) passing through the filters is measured. High concentrations of com-pounds not volatilized during the fusing operation absorb a portion of the fluorescent light. (This effect is known as "quenching".) Since a given amount of an interfering compound absorbs a fixed percentage of the uranium fluorescence the quenching effect may be determined by making two determinations, the first on an unspiked portion of the sample and the second on a portion of the sample spiked with a known amount of uranium.

Time required per determination: 45 minutes.

Systematic error: The fluorophotometer results may "drift" over extend-ed operating periods. The drift is eventually detected and the instrument is reset so that there is very close to zero systematic error. It is felt that the drifting may be detected and corrected by the time it has amount-ed to a 10% discrepancy.

Precision (99% limits): Better than ± 20%.

Sample size: The accuracy and precision figures listed above may be obtained if the sample contains from 0.01 to 1 microgram of UNH.

16. Uranium Isotopes by the Mass Spectrograph

Application: The mass spectrometer used for the analysis of the U-235 concentration in recovered uranium is suitable for the determination of

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a wide range of U-235:U-238 ratios. However, it is not advisable to handle on a single instrument samples which vary over a range of isotopic concentrations exceeding a few tenths per cent, since in such cases, the instrument exibits a "memory effect", whereby each result is biased in the direction of the concentration of the preceding sample (a small portion of the sample remains in the system). All recovered Redox and underground-stored uranium is not expected to vary in U-235:U-238 ratio by more than a few tenths of a per cent.

<u>Description</u>: The sample containing the uranium (about 1 g.) is first converted to U_3O_8, which is in turn converted to uranium hexafluoride by heating in a tube furnace to about 400°C. with cobalt trifluoride. The UF_6 evolved is collected in a nickel condenser in a liquid nitrogen bath. The UF_6 is then volatilized and introduced at a controlled rate into the sampling system of the mass spectrometer where it is directed by a slit through an ionizing chamber. A small fraction of the UF_6 is converted to UF_5^+ ions (masses 330 and 333). These ions are accelerated as they pass through plates charged with high voltages. The accelerated ions then pass through the mass spectrometer tube along curved paths under the influence of a strong magnetic field. Because the isotope ions differ in mass, these curved paths diverge so that the two species UF_5^+-330 and UF_5^+-333, are appreciably separated after passing through the tube. They are then collected at suitable electrodes and the resulting currents are amplified providing a measurement of the relative concentrations of the ions. From the relative ion concentrations the U-235:U-238 ratio in the original sample may be caluclated.

<u>Time required per determination</u>: Elapsed time -- 2 hours.
Operator time -- 60 to 90 minutes.

<u>Systematic error</u>: Although the true value is not known it is believed to be well within the 99% precision limits.

<u>Precision (99% limits)</u>: Better than ± 0.005% U-235 in the region of natural abundance (U-235 = 0.7%).

<u>Sample size</u>: The sample should be chosen such that one gram of uranium is available for each analysis.

17. <u>Uranium by the X-Ray Photometer</u>

<u>Application</u>: The method is used for either organic or aqueous solutions (e.g. RCU Sampler, UN Tank, and Tanks X-1 and X-2) containing high UNH concentrations (5 to 1000 g./l.). Since the absorption of X-rays increases very rapidly with increasing atomic number the sample to be analyzed must contain an appreciable concentration of only one element of high atomic number.

<u>Description</u>: X-rays are passed through a fixed depth of sample solution and a portion of the beam, depending upon the concentration of high atomic number elements in the sample, is absorbed. The same X-rays are passed through varying known thicknesses of aluminum which have been

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been calibrated against known standard uranium concentrations until the absorption of the aluminum matches the sample absorption.

Time required per determination: 20 minutes.

Systematic error: Minus 1 to plus 1%.

Precision (99% limits): ± 1 to 2%.

Sample size: The minimum volume required for routine analysis varies with the uranium concentration. Solutions containing more than 100 g. UNH/l. are diluted to provide enough volume of 5 to 100 g.UNH/l. solution to fill a photometer sample cell holding 3 ml. Larger cells may be used if sufficient sample is available. Three ml. of HW No. 4 Flowsheet RCU containing 66 g.UNH/l. is required.

D. RADIOCHEMICAL DETERMINATIONS

The results of the various radiochemical determinations described in this section are reported in counts/minute for methods based upon beta counting on a BGO counter and in amperes for methods based upon gamma counting by the Shonka Chamber. Conversion of the Shonka Chamber amperes to curies is discussed in D4 below.

The counts/minute obtained by beta counting methods on a BGO Counter may be converted approximately to "countable" curies by dividing by the geometry of the counter (approximately 0.067 on the second shelf of a BGO Counter) and by the curie conversion factor $(3.7 \times 10^{10}$ disintegrations/(sec.)(curie)). Further conversion of the "countable" curies to absolute (or theoretical) curies is discussed in Chapter II.

1. Cerium -- Oxalate-Iodate Precipitation Method

Application: The method is suitable for any Uranium Recovery Plant sample.

Description: Cerium activity is separated from other fission-product activities by two precipitations. Cerium (including non-radioactive cerium added as a carrier) is first precipitated with oxalic acid. The washed oxalate precipitate is dissolved in nitric acid; the cerium is oxidized with bromate; and ceric iodate is precipitated. The separated iodate is destroyed with oxalic acid and cerium is reprecipitated as the oxalate for mounting and counting. Since the radioactivity of the praseodymium daughter of cerium is measured, the mounted sample must be allowed to stand approximately two hours before counting to permit the cerium-praseodymium transient equilibrium to be reached. The "hard" beta radiation passing through a 355 mg./sq.cm. aluminum absorber is measured on a standard BGO counter. Corrections are made for the carrier recovery which is determined from the weight of the final oxalate precipitate and the weight of cerium carrier originally added.

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Time required per determination: 40 minutes operator time, 2-1/2 hours elapsed time.

Systematic error: (500 to 5000 counts/minute) Plus approx. 10%.

Precision (99% limits): For 500 to 5000 counts/minute, ± 10%.

Sample size: If possible, for the above systematic error and precision, the sample should be chosen so that 500 to 5000 counts/minute are registered on the counter. For an RAF sample prepared from 2-yr. aged waste, the smallest accurately measured sample volume (0.005 ml.) contains far more cerium (3×10^5 counts/minute) than required for the analysis. Consequently the sample is initially diluted and an aliquot is chosen to give the required 500 to 5000 counts/minute.

2. Cesium -- Chloroplatinic Acid Method

Application: Radiocesium in all Uranium Recovery Plant samples may be determined by this method.

Description: Radiocesium and a carefully measured quantity of inactive cesium "carrier" remain in solution when interfering fission products are removed by scavenging with ferric hydroxide formed in the solution. Cesium in the supernate is then precipitated as the chloroplatinate from acid solution. The cesium chloroplatinate precipitate is then washed, mounted on a weighed brass counting disc, dried, and weighed. From the weight of cesium chloroplatinate the cesium recovery may be calculated. The beta emission of the radiocesium is then determined using a standard BGO counter.

Time required per determination: 45 minutes.

Systematic error: Approximately minus 10% above 1000 counts/minute.

Precision (99% limits): Above 1000 counts/minute, better than ±10%.

Sample size: To obtain the systematic error and precision indicated above the sample should contain approximately 1000 to 5000 cesium counts/minute. For an RAF sample prepared from 2-yr. aged waste, the smallest accurately measured sample volume (0.005 ml.) contains more cesium (5×10^4 counts/minute) than required for the analysis. Therefore, the sample is initially diluted and an aliquot is chosen to give the required 1000 to 5000 counts/minute.

3. Gross Beta by BGO Counter

Application: The BGO (Beta-Gamma-Offner) counter may be used for the determination of total coutable beta radiation. Gamma radiation is counted along with beta but the proportion of gamma counts is generally only a small fraction of the total and therefore may be neglected. However, if the gamma counts are a large percentage of the total counts, the gamma count must be determined and beta calculated by difference.

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The counter may also be used for gross gamma determinations, but for most routine gross gamma analyses the Shonka chamber is used. Only beta radiation capable of passing through a 20 mg./sq.cm. aluminum absorber (i.e., 0.15-M.e.v. beta or above) is counted.

Description: The sample is pipetted onto a watch glass, evaporated to dryness and counted on a BGO counter, with a 20 mg./sq.cm. aluminum absorber interposed between the sample and the counter.

Time required per determination: 45 minutes.

Precision (99% limits): Approximately ± 4 to 2% for a five-minute count of a sample containing 1000 to 5000 counts per minute.

Sample size: To obtain the above precision, the sample size should (if possible) be such that 1000 to 5000 counts/minute are received by the counter. (See the discussion of counting precision at the beginning of this chapter.) One milliliter of RAF solution (prepared from 2-yr.-aged waste) contains approximately 2×10^8 counts/minute. Therefore, to obtain the desired number of counts, a small volume (less than 0.1 ml.) is diluted and an aliquot is taken to give the required number of counts. One liter of 0.13 $\underline{M}$ UNH RCU solution contains approximately 2×10^5 beta counts/minute.

4. Gross Gamma by Shonka Chamber

Application: Gross gamma radioactivity may be determined for all samples which contain from 0.02 to 1000 microcuries of gamma radiation.

Description: A sample -- gas, liquid, or solid -- is placed in the well of the ionization chamber. The gamma radiation of the sample passed through the inner wall of the chamber into high pressure argon gas surrounding the chamber producing ionization of the gas. The ionization causes an increase in the current flowing between an electrode in the gas and the ionization chamber wall. The current is measured and recorded using a vibrating-reed electrometer and recording potentiometer, and may be compared with the ionization current produced by standard radium samples.

Time required per determination: Less than 10 minutes.

Systematic error: The results obtained by the Shonka counter are reported in terms of current flow, or in terms of the equivalent curies of standard radium represented by the registered current obtained during calibration. This method of reporting does not give the absolute curies (3.7×10^{10} disintegrations/second) present in the sample unless the radiation spectrum and the decay mechanisms of the sample are similar to those of the radium standard. Although it is not possible to assign exact values for the conversion of the reported current to absolute curies, the following are approximate values for gamma rays of specific monochromatic energies:

Measured Shonka Current (amps)[a]	Equivalent Radium[b] Millicuries	Disintegration Per Second	Absolute Millicuries for Specific Monochromatic Energies				
			0.1 M.e.v.	0.2 M.e.v.	0.6 M.e.v.	1.0 M.e.v.	3.0 M.e.v.
1×10^{-13}	1.7×10^{-5}	6.3×10^2	4.9×10^{-5}	4.0×10^{-5}	2.1×10^{-5}	1.4×10^{-5}	7.6×10^{-6}
1×10^{-12}	1.7×10^{-4}	6.3×10^3	4.9×10^{-4}	4.0×10^{-4}	2.1×10^{-4}	1.4×10^{-5}	7.8×10^{-5}
1×10^{-11}	1.8×10^{-3}	6.6×10^4	5.4×10^{-3}	4.0×10^{-3}	2.1×10^{-3}	1.5×10^{-3}	8.1×10^{-4}
1×10^{-10}	1.8×10^{-2}	6.6×10^5	5.4×10^{-2}	4.0×10^{-2}	2.2×10^{-2}	1.5×10^{-2}	8.3×10^{-3}
1×10^{-9}	1.9×10^{-1}	7.0×10^6	5.4×10^{-1}	4.2×10^{-1}	2.2×10^{-1}	1.5×10^{-1}	8.5×10^{-2}

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[a]600 volts potential on the ionization chamber.

[b]Elemental radium-226 in equilibrium with daughter elements.

Precision (99% limits): Varies with the gamma activity of the sample, from ± 0.2% for 100-microcurie samples to approximately 10% for 0.02-microcurie samples.

Sample size: The ionization chamber well will hold any size sample up to approximately 40 ml. However, if possible, the sample size should be selected so that the gamma radiation of the sample is between 0.1 and 100 microcuries. One milliliter of RAF solution (prepared from 2-year-aged waste) contains approximately 400 microcuries of gamma radiation. Therefore, an undiluted 0.1 ml. RAF sample can be measured in a Shonka chamber.

5. Plutonium -- Direct Evaporation Method

Application: Plutonium (plus other alpha emitters such as americium and curium) may be determined for those streams, both organic and aqueous, containing little or no uranium (e.g., cribbable condensates). If the uranium-to-plutonium ratio is less than 1×10^7 the uranium concentration should be determined and the equivalent uranium counts should be subtracted from the result obtained by this method. The sample should be essentially free of salts (less than 0.25 mg.) which are not volatilized when the sample is evaporated to dryness, because such salts absorb a portion of the plutonium alpha radiation.

Description: The sample is transferred directly to a platinum disc and a small amount of lanthanum fluoride is precipitated on the disc to insure even distribution of the plutonium over the surface of the disc. The precipitate is then evaporated to dryness and the sample is counted on a standard alpha counter.

Time required per determination: 45 minutes.

Recovery: Approximately 100%.

Sample size and precision: Sample size is dependent upon the plutonium concentration and the precision required of the determination. For a discussion of these factors see the beginning of the chapter. For 20% counting precision the sample chosen should contain sufficient plutonium (approximately 0.001 microgram) to register approximately 50 alpha counts/minute on a standard ASP counter during a 5 minute counting period. A 2-milliliter sample of condensate of the cribbing tolerance (0.5 microgram/liter) contains the necessary 50 counts/minute.

6. Plutonium -- Fluoride Precipitation Method

Application: This is a radiochemical method which may be used for the determination of Uranium Recovery Plant streams containing relatively large plutonium concentrations (e.g., RAF, RAW).

Description: Pu(III) and Pu(IV) are separated from interfering substances by "carrying" the plutonium on a lanthanum fluoride precipitate formed in the sample solution. The precipitate is centrifuged and washed

before counting in a standard alpha counter. If the total amount of Pu is to be determined by this method, the sample must first be treated with a reducing agent ($NH_2OH \cdot HCl$) to convert the Pu(VI) to a lower valence state.

Time required per determination: 90 minutes.

Recovery: 99 to 99.5%.

Sample size and precision: Sample size is dependent upon the plutonium concentration and the precision required of the determination. These factors are discussed at the beginning of the chapter. For 1 to 2 per cent counting precision the sample size should be regulated so that during a 5-minute counting period 3000 to 15000 counts/minute (approximately 0.04 to 0.2 micrograms of plutonium) are registered on the counter. A 0.1 ml. sample of RAF may contain approximately 1000 plutonium alpha counts/minute.

7. Plutonium -- Low-Level Plutonium by Fluoride Precipitation

Application: This method is used for the determination of low plutonium concentrations in the presence of relatively high uranium concentrations (e.g., RCU, Concentrated UN Solution, UO_3). The method may be used for analyzing organic samples if a small amount of acetone is added to the sample to increase its solubility in water.

Description: An initial lanthanum fluoride precipitation is made to separate the plutonium from the bulk of the uranium and other interfering ions. The precipitate, which has "carried" the plutonium and a slight amount of uranium with it, is then metathesized with potassium hydroxide to form lanthanum hydroxide. This $La(OH)_3$ precipitate (and the "carried" plutonium) is dissolved with concentrated nitric acid and again treated with HF to form a second lanthanum fluoride precipitate. The washed LaF_3 is mounted on a platinum disc, dried, and counted on a standard alpha counter.

Time required per determination: 180 minutes.

Recovery: Approximately 95%.

Sample size and precision: Sample size is dependent upon the plutonium concentration and the precision required of the determination. These factors are discussed at the beginning of this chapter. Generally only fair precision will be required for these low-level Pu streams. For approximately 20 per cent counting precision the sample selected should register approximately 40 counts/minute on the standard counter for a 5 minute counting period. A 0.02 ml. sample of RCU containing approximately 3×10^{-7} g.Pu/liter is required to produce the required 40 Pu alpha counts/minute.

8. Strontium -- Fuming Nitric Acid Method

Application: This method is suitable for all Uranium Recovery samples.

Description: Strontium activity is separated from other fission products by a series of precipitations. Strontium (including non-radioactive strontium added as carrier) is first precipitated with sulfuric acid. The precipitate is digested, centrifuged, and washed with water. The $SrSO_4$ is next metathesized to $SrCO_3$. After centrifuging and washing the precipitate is dissolved in a small amount of 6 $\underline{N}$ HNO_3. Strontium nitrate is precipitated by the addition of fuming nitric acid, then centrifuged and dissolved in water. Ferric ion is added to the solution and a portion of the interfering fission-product activity is carried from solution on $Fe(OH)_3$ precipitate. The centrifuged supernate is heated and $SrC_2O_4 \cdot H_2O$ is precipitated upon the addition of saturated ammonium oxalate. The solution is filtered and the precipitate is washed successively with water, 95% ethanol, and ether. The dry, weighed precipitate is counted on a standard BGO counter. From the recovery of the inactive carrier added originally and the radioactivity of the final precipitate the strontium radioactivity in the original sample may be calculated.

Time required per determination: 1-1/2 hr.

Recovery: Approximately 80%.

Precision (99% limits): Better than ± 20% (estimated for a sample containing 500 to 5000 counts/minute).

Sample size: For the above stated precision and recovery the sample size should be chosen such that 500 to 5000 beta counts/minute are registered on a standard BGO counter. A milliliter of RAF sample prepared from 2-yr.-aged waste contains approximately 2 x 10^7 strontium beta counts/minute. Therefore, the sample is initially diluted and a suitable aliquot is taken analysis.

9.   **Ruthenium -- Direct Reduction Method**

Application: Radioruthenium may be determined in all Uranium Recovery samples by this method.

Description: A known amount of inactive ruthenium carrier is added to the sample which is subsequently reduced to ruthenium metal with magnesium in a strong hydrochloric acid solution. The metal is filtered, dried, and weighed. The "hard" beta emission passing through a 355-mg./sq.cm. aluminum absorber is measured on a standard BGO counter. The effect of interfering activity of zirconium and cerium is minimized by adding inactive zirconium and cerium "holdback" carriers to the sample so that only a small percentage of the radioactive zirconium and cerium is carried with the ruthenium. From the ruthenium recovery and the beta activity of the ruthenium metal the active ruthenium in the original sample may be calculated.

Time required per determination: 30 minutes.

Recovery: Approximately 101% for high counting rates (1000 to 7000 counts/minute). Approximately 120% for low counting rates (less than 1000 counts/minute).

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Precision (99% limits): ± 10%.

Sample size: For the above counting precision the sample should emit approximately 1000 to 7000 ruthenium "hard" beta counts/minute. A 5-microliter sample (the smallest accurately measured sample volume) of RAF (prepared from 2-yr.-aged waste) contains the radioactivity (approximately 1×10^4 Ru beta counts/minute) required for the determination.

10. Zirconium -- Barium Fluozirconate Method

Application: This method may be used for the determination of radio-zirconium in all Uranium Recovery Plant streams.

Description: An accurately measured quantity of inactive zirconium carrier solution is added to the sample. The sample acidity is adjusted with nitric and hydrofluoric acids before lanthanum fluoride is precipitated from the solution. The lanthanum fluoride scavenges a large portion of the radioactive rare-earth elements with it. Barium nitrate is then added to the separated supernate and barium fluozirconate is precipitated. The precipitate is centrifuged, washed with a weak $HF-Ba(NO_3)_2$ solution, and dissolved in boric and nitric acids. After inactive niobium "holdback carrier" has been added to the solution to minimize radioniobium carrying, barium fluozirconate is reprecipitated, centrifuged, washed, dried, weighed, and counted in a Shonka chamber. From the zirconium recovery (calculated from the weight of the dried barium fluozirconate precipitate and the weight of the inactive zirconium added) and the gamma activity of the zirconium metal the active zirconium in the original sample may be calculated.

Sulfates present in the RAF and RAW samples are precipitated as $BaSO_4$ when barium fluozirconate is precipitated during the determination. However, the barium fluozirconate to barium sulfate weight ratio is generally so great (10 or better) that the barium sulfate weight will have no significant effect on the chemical yield reported for the method.

Time required per determination: 30 to 40 minutes.

Recovery: Approximately 100%.

Precision (99% limits): Approximately ± 20%.

Sample size: To attain the above-stated over-all precision the sample should be selected so that the counting precision is within ± 4%. To achieve this counting precision 2000 or more gamma counts/minute are registered on the BGO counter for a 5-minute counting period. The required 2000 counts/minute are contained in approximately 0.1 ml. of RAF prepared from two-year-aged stored waste.

If the Shonka counter is used for the determination a current of approximately 1×10^{-11} amperes representing approximately 1×10^{-3} milli-curies of Zr gamma activity is required to achieve ± 4% counting precision. One ml. of RAF prepared from 2-year-aged stored waste provides the required Zr activity.

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PART V: SAFETY

CHAPTER XXI. HEALTH PROTECTION FROM RADIATIONS

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CHAPTER XXI. HEALTH PROTECTION FROM RADIATIONS

A. NATURE OF RADIATIONS

Nuclear radiations are invisible and undetectable by the unaided senses. The harmful physiological effects of excessive dosages of nuclear radiations make certain protective measures necessary. For a brief review of the physiological effects of radiations, the reader is referred to the Redox Technical Manual (HW-18700), Chapter XXII.

The radiations emitted by materials in the separation processes are alpha particles, beta particles, and gamma rays. Neutrons are emitted only during pile reaction and no neutron radiation hazard is encountered in separation plants.

1. Alpha Particles

Alpha particles are helium nuclei of mass four and positive charge two. They are ejected spontaneously by the nuclei of uranium and plutonium atoms, but not by fission-product elements. Because of the large mass and charge of the alpha particle its penetrating power is very low. For example, the alpha particles from uranium are completely stopped by about 1 inch of air, 0.001 inch of aluminum, or 0.0001 inch of lead. Alpha particles present an important hazard only when the emitter is taken into the body.

2. Beta Particles

Beta particles are fast electrons. They carry a negative charge of one unit and are emitted with energies rarely exceeding 3 M.e.v. Their penetrating power is rather low. (2 M.e.v. beta are completely stopped by about 23 ft. of air or about 1/8 inch of aluminum.) The beta radiation hazard assumes importance only when the observer is directly exposed to the source or when the emitter is taken into the body. Under exceptional circumstances the secondary radiation produced upon absorption of beta particles in matter (Bremsstrahlung, or "slowing-down radiation") may also represent a hazard.

3. Gamma Rays

Gamma rays are electromagnetic rays with wave length roughly one millionth that of visible light. Unlike alpha and beta particles, gamma radiation has no definite range in matter but is absorbed exponentially. The intensity of a beam of 2 M.e.v. gamma radiation is reduced ten-fold by passage through 1300 ft. of air, 20 inches of water, 8.5 inches of concrete, 8 inches of aluminum, or 1.7 inches of lead. Reduction of the intensity of this radiation by a factor of 100 is obtained by using a shield of 3.4 inches of lead. Although gamma rays are less damaging than alpha or beta radiation, quantity for quantity, they are a major problem because they penetrate so deeply.

B. **CURRENT PERMISSIBLE RADIATION EXPOSURE LIMITS**

For any systematic program of radiation control it is necessary to know precisely what quantities and rates of exposure can be permitted. The permissible radiation exposure limit is the quantity of radiation which a human can withstand day after day without perceptible damage to the body. Because of the lack of full, exact knowledge, the permissible exposure limits at Hanford Works are conservatively set and frequently reviewed in the light of new information.

For the current permissible radiation exposure limits, reference is made to the Redox Technical Manual (HW-18700), Chapter XXII.

C. **METHODS OF MONITORING**

In addition to the design provisions for safety from radiation, notably shielding and safeguards against leakage of radioactive material, incorporated in the design of the Uranium Recovery Plant and its equipment, a thorough and constant program of radiation monitoring is maintained with a view to avoiding accidental overexposure of personnel.

The chief items requiring constant and careful monitoring are included in five categories: (a) operating areas and equipment; (b) personnel; (c) ventilation air; (d) stack gas, and (e) environs.

The following discussion outlines the radiation monitoring methods used in connection with the Uranium Recovery Plant.

1. **Monitoring of Operating Areas and Equipment**

Although the equipment and facilities provided are adequate for handling the radioactive process solutions under normal operating conditions, in the event of operational accidents or the need to enter any of the equipment cells or areas for inspection or maintenance, it is necessary that the areas and equipment be surveyed for the presence of radioactive materials. In addition, surveys of all operating areas of the plant are made on a routine basis in order that contamination can be removed, and radiation confined. The techniques of decontamination are discussed in Chapter XXIII.

1.1 **Health Monitor (HM) stations**

Fixed monitor stations which measure and record gamma radiation (and beta if no shields are used) levels in the uranium recovery facilities are located as follows:

221-U Building: (Reference drawing: SK-2-6091)

Canyon, chambers are placed at Sections 1 through 19 inclusive (odd numbers only). These ionization chambers are equipped with shields.

Operating gallery, chambers are placed above the panel boards corres-ponding to Sections 4, 7, 9, 11, 13, 16, and 19. There are no shields on these chambers.

Pipe gallery, chambers are located at Sections 3, 7, 13, and 19.

In addition, ionization chambers are located in the SWP change room and in the crane cab. A complete installation consists of an ionization chamber, located as noted above, a Beckman RXG amplifier, and a recorder, located in the dispatcher's office.

224-U Building:

There are four ionization chambers located in Building 224-U. Two are above the panel boards corresponding to Cells B and D and two are located in the pipe gallery.

241-WR Diversion Vault:

There are four ionization chambers located adjacent to the tanks in the 241-WR Vault. It is possible to read the radiation level of the tanks from an instrument located at the head of the stairs in 241-WR without en-tering an SWP zone.

241-U Retention Basin:

Two semi-portable ionization chambers located on booms are provided for monitoring the Retention Basin.

Radiation intensities which can be detected reliably are limited by the fixed volume of the ionization chamber and by the Beckman amplifier, which provides six sensitivities permitting measurement of radiation intensities from 0.03 mr./hr. to 300 r./hr. The BM instruments are cali-brated weekly by the Radiation Monitoring Unit.

1.2 Portable survey instruments

The most common portable survey instruments (six in all) are briefly described in Chapter XXI of the Redox Technical Manual (HW-18700).

The value of any radiation survey is dependent on the judgement of the surveyor in selecting an instrument, making the survey, and interpreting the data. If quantitative measurements are made, survey instruments must be used in substantially the same manner as they were calibrated. With regard to alpha measurements, the short range of the particles requires that the instrument be used as close as possible to the area being exam-ined and with no absorber (paper, film of water, etc.) between the source and the sensitive element.

2. Monitoring of Personnel

The subject of monitoring of personnel is discussed in Chapter XXI of the Redox Technical Manual under the following subheadings:

(a) Special Hazard Bulletins (2.1)
(b) Personnel exposure monitoring (2.2)
(c) Monitoring of personnel leaving a Radiation Danger Zone (2.3)

3. Ventilation Air Monitoring

A vacuum air sampling system is installed at various positions in the Uranium Recovery Plant for obtaining air samples. The samples of air are drawn through filter paper which filters out and retains particulate matter which was suspended in the air stream. Radioactive gases such as xenon or krypton pass through the filter paper and are therefore not capable of being measured.

Particulate contamination collected on filters is measured by its radioactivity. When ashless filter paper is used (Whatman 41), the paper is digested with acid, and the solution is evaporated to dryness. Radiation counts are taken on the solid residue by means of a Mica Window Counter (BGO). When the sample is taken on asbestos filter paper (Chemical Warfare Service Type 6), the Horizontal Pig Air Sample Counter or Mica Window Counter is used for determining the beta and gamma activity. Readings of activity should be made within an hour after sampling. If the beta count indicates a high concentration of beta emitters, additional counts are taken to estimate the half-life.

The standard Parallel Plate Chamber or the Long Ton Chamber is used for counting the alpha activity which is emanated from radon, thoron, their daughters, and uranium. Two counts are taken, the "six-hour" count and the "twenty-four-hour" count. From these two counts, the background due to radioactivities controlled by the ThB decay rate can be obtained and the activity of the uranium can be calculated. If both plutonium and uranium are possibly present in the air, their concentrations can be determined either by chemical analysis of the contamination collected on the filter paper or by range determinations on the alpha particles. Respiratory protection is required if the radioactivity determined from an air sample indicates air contamination in excess of one of the following working limits:

Fission products (mixed)-- 1×10^{-9} microcurie/cu.cm.
Plutonium------------------ 3×10^{-11} microgram/cu.cm.
Uranium-------------------- 3×10^{-5} microgram/cu.cm.

Provision for air sampling stations in the 221-U Building has been made by extending Saran tubing through existing spare piping (connectors 88 and 90) leading from the operating gallery into the canyon at Sections 3 through 20 inclusive. This arrangement permits drawing an air sample through one line and exhausting the filtered air back into the canyon through the other line by means of a portable air sampler pump.

Building 224-U is equipped with four permanent air sample stations, one before the bag filters, two (one in each line) after Bag Filters X-11-1 and X-11-2, and one located near the top of the exhaust stack. In addition, two portable units are provided for obtaining air samples within the building.

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4.   Stack Gas Monitoring

Air from the Uranium Recovery Plant (which is exhausted through
Ventilation Stack, 291-U) is monitored for particulate activity. An
exhaust air sample station is located near the exhaust duct before it
enters the sand filter. In addition, air samples may be obtained from
sample ports located near the two inlets to the sand filter (duct from
221-U Building and duct from 241-WR Diversion Vault).

There are two air samplers on the Stack. One is located four feet
below the top of the Stack, the other about twenty feet above grade, near
the bottom of the Stack.

5.   Environs Monitoring

Stations are maintained both on and off the project by the Radiation
Monitoring Unit for the purpose of determining the amount of radioactive
materials (i.e., particulate matter and iodine) released into the environ-
ment by operations at Hanford Works. The distribution of radiomaterials
in the air, water, and earth around the project is mapped on a monthly
basis, and radioactivity measurements at locations outside the project are
recorded.

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PART V: SAFETY, continued

CHAPTER XXII. SHIELDING

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Radioactive fission products are formed during irradiation of the uranium slugs in the piles. The level of emitted radioactivity gradually decreases with time as discussed in Chapter I. Since this radioactivity is harmful to personnel, they must be protected from it by distance or by intervening shielding materials. As discussed below, the vessel walls absorb the alpha and beta radiation, but a considerable thickness of shielding material is required to reduce the very penetrating gamma rays to a harmless level.

Irradiated uranium emits three principal types of radioactivity: alpha and beta particles, which are discussed in Section A, below, and gamma rays, or photons, which are discussed in Section B of this Chapter.

A. ABSORPTION OF ALPHA AND BETA PARTICLES

1. Alpha Radiation

The isotopes of uranium and some of the transuranic elements which are formed during irradiation emit alpha particles, which are helium nuclei. Due to their large mass (compared with electrons or photons) and double charge, the ion production per unit length of path (i.e., the rate of energy absorption by matter through which the particle passes) is high. This means that the total energy of the particle is absorbed in passing through a relatively small amount of matter, the distance traveled being known as the range in that material. For example, the range of the 4.18 M.e.v. (Million electron volts) alpha particle from U^{238} is approximately 1 inch in air, 0.001 inch in the dead layer of skin, 0.0006 inch in aluminum, and 0.00035 inch in lead. Because of the above-mentioned short range of alpha particles, alpha radiation is an important hazard only when the alpha emitter is taken into the body. No shielding is required to protect personnel from external alpha radiation.

2. Beta Radiation

Fission products and some of the transuranic elements which are formed during irradiation, as well as some of the daughter elements of uranium, emit electrons known as beta particles, or beta rays. Beta particles do not produce as many ions per unit length of path as alpha particles and, therefore, are more penetrating than alpha particles which have the same initial energy. For example, the 2.3 M.e.v. beta particle from either UX_2 or Rh^{105} has a range of approximately 25 feet in air or 0.15 inch in aluminum. Beta particles do not normally penetrate container walls. They constitute a radiation hazard only when taken into the body, or when the individual is exposed directly to the source, such as the exposed surface of a solution containing beta emitters, or bare radioactive metal.

B. THE GAMMA RAY ATTENUATION PROBLEM

Most fission products and transuranic elements which are formed during irradiation, as well as most isotopes of uranium and its daughter elements, emit a very penetrating form of radiation known as gamma rays. Gamma rays are electromagnetic radiations, or photons, originating from a nucleus. Unlike alpha and beta particles, gamma rays have no definite range in matter, but are absorbed approximately according to an exponential law on passing through the material. The range of gamma ray energies of interest in the 200 Areas is from 0.1 to 2.3 million electron volts (M.e.v.).

Attenuation (i.e., intensity reduction) of gamma rays may be accomplished by distance, by passage through matter, and by scattering. The various attenuation mechanisms are considered in Chapter XXII of the Redox Technical Manual, HW-18700.

The maximum permissible radiation level for uncontrolled zones, such as the operating gallery in 221-U Building, is 0.1 mr./hr. (milliroentgens per hour). For controlled zones, such as the canyon deck in Building 221-U, the maximum permissible radiation level is 1 mr./hr.

The table below lists gamma ray intensities and required attenuation factors corresponding to typical radiation sources in the Uranium Recovery Plant. Attenuation factors listed are those required for uncontrolled zones.

Gamma Ray Intensity

Source	Approximate Distance, Tank to Observer, Ft.	Intensity R./Hr.[a]	Attenuation Factor Required
RAF Feed Tanks	10	10[b]	10,000
RAW Waste Receivers	10	10[b]	10,000
101-U Waste Storage Tank	5 to 10	0.5 to 1.0[c]	500 to 1000
UO$_3$ Pot	1	0.0002	2

Notes:

(a) Intensity with no intervening shield. One roentgen of radiation liberates 83.8 ergs of energy in one gram of air.

(b) Computed for material "cooled" for 2 years.

(c) Measured value, material stored 5 to 6 years.

Methods of calculating the amount of gamma ray attenuation attained by a specified thickness of shielding material are presented in Chapter XXII of the Redox Technical Manual.

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C. URANIUM RECOVERY PLANT SHIELDING

1. Uranium Removal Facilities

Pipe lines which carry underground wastes from the waste storage tanks (and lines which return supernate for sluicing operations) are encased in a concrete tunnel with 8-inch-thick sides and a 10-inch or thicker top. The concrete tunnel is covered with earth to a minimum depth of about 2-1/2 feet.

A minimum thickness of about 6 feet of earth over the waste tanks reduces the radiation level to safe limits.

2. TBP Plant, Building 221-U

The 221-U Building was originally designed to house a bismuth phosphate (plutonium extraction) plant; consequently, shielding in the building is of massive construction. In general, shielding was designed so that the gamma-ray dosage rate received in any populated area was less than about 0.1 mr./hr. when a bucket of "cooled" uranium slugs was present in the building. This amount of shielding is greater than that required for the TBP Plant, since the feed stream for the TBP process (aged underground wastes) will emit much less intense radiation (approximately 200-fold less radiation intensity for waste aged 2 years than for material aged only 40 days).

The wall of the canyon (221-U Building) on the side opposite the operating gallery is not less than five feet thick from the ground up to a height of 26 feet above the canyon deck level. The walls on both sides of the canyon taper from a thickness of 3 feet at this point to 4 feet at the roof, and the roof, for structural reasons, tapers from a thickness of 4 feet at the sides to 3 feet at the center. On the operating gallery side of the canyon, the outside building wall is 3 feet thick from the ground to the crane cabway, where it is 5 feet thick up to 26 feet above the canyon deck level. The lower part of the wall shields personnel outside the building or in adjacent buildings from direct gamma radiation at times when "hot" process solution is present in the canyon. The upper part of the wall and the roof eliminate "sky shine" or radiation scattered from the air above the canyon, which would otherwise produce a hazard in the neighborhood of the building.

The various process vessels are located in a row of cells which are sunk below deck level and normally shielded by concrete cell covers 6 feet thick. Each cell cover is built up of four concrete blocks to facilitate handling. The recess into which the cover fits has stepped sides, and the adjoining faces of the individual blocks are also stepped to eliminate narrow beams of radiation which otherwise would escape from the cells. Exceptions to the above statements occur in the concentrator cells (11, 13, 15, 17, and 19) and in the two cells containing the two RA Columns (34 and 38). Cell covers for the concentrator cells are 2-1/2 feet in thickness in order to provide more height within the cells. This thickness of concrete is sufficient to reduce gamma radiation to a maximum value of 6.25 mr./hr. the cell cover blocks. The two cells containing the two

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RA Columns have a raised cover block, "dog-house", which is two feet in thickness and the top of which is four and a half feet above the canyon deck. The raised cover blocks allow sufficient head-room for the RA Columns.

Radioactive solutions are transferred from one cell to another by way of a pipe trench running the length of the canyon. The pipe trench is covered by stepped concrete covers, 2 feet thick, similar to those used on the cells. Significant amounts of radiation are present in the canyon only when the covers have been removed from cells or the pipe trench. At all other times the canyon may be entered for the purpose of taking samples or maintaining such equipment as is accessible.

Labyrinths in the 5-foot concrete wall on the pipe trench side of the canyon provide access to the deck. The labyrinth walls are 5 feet thick as far as the second bend. From this point to the outside entrance the intensity of the scattered radiation is low enough so that walls 1 foot thick are adequate.

The wall which shields the various galleries is 9 feet thick opposite the pipe gallery and 7 feet thick opposite the operating gallery. This thickness of concrete is sufficient to attenuate gamma intensity well below 0.1 mr./hr., which is the permissible upper limit for an uncontrolled zone. Pipes which run through these walls are curved to minimize radiation leakage. The pipe gallery handles only non-radioactive materials (radioactive process solutions are transferred in the pipe trench on the other side of the canyon), and the piping is designed to minimize the chance of sucking radioactive solutions back into the pipe gallery. The few suckbacks that have occurred in bismuth phosphate plant operation have been promptly detected and remedied. The roof of the operating gallery, which also forms the floor of the crane cabway, is 4 feet thick. This thickness is more than adequate inasmuch as this floor is exposed only to radiation which has been scattered from the canyon ceiling. The cabway is entered through a row of labyrinths on the operating gallery side of the building.

The crane cab is shielded from direct gamma radiation by the concrete parapet behind which it runs. Protection against scattered radiation is afforded by the steel shielding of the cab, which is 4-1/2 inches thick on the top and upper part of the sides, 3 inches thick on the lower part of the sides, and 1-1/2 inches thick on the bottom. The cab is entered through steel doors 3 inches thick. Steel is used in this structure rather than lead because of the danger that lead might eventually sag and open up crevices through the shield.

Sampling devices are located in boxes shielded with 4 inches of lead and sunk flush with the canyon deck level.

Ionization chambers which indicate the activity of process solutions are located in wells which run from deck level down to the level of the process vessels. These wells are plugged to stop the radiation scattered up the tube.

3. Uranium Conversion Plant, Building 224-U

The very low level of radioactivity associated with the uranium processed in the 224-U Building does not require any special shielding for radiation protection of personnel. However, the level of gamma radiation intensity from equipment within the building is calculated to be between 0.1 and 1 mr./hr. with the exception of the UO_3 shipping drums, which have a surface intensity of ca. 2.7 mr./hr.; therefore, it is necessary to class the area as a controlled zone.

In UO_3 storage facilities outside the 224-U Building gamma radiation intensities may be in excess of 1 mr./hr. (up to about 5 mr./hr.), but personnel will not ordinarily be required to work in those areas, except for appropriately short periods.

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CHAPTER XXIII. DECONTAMINATION OF SURFACES

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CHAPTER XXIII.   DECONTAMINATION OF SURFACES

A. INTRODUCTION

1. General

Surface decontamination will find application in the Uranium Recovery Plant for the removal of radioactivity from operating equipment and working areas in order that personnel may approach the equipment to make necessary maintenance changes. The total radioactivity per ton of uranium entering the plant will be less than that entering the Redox Plant by a factor of approximately 20 to 100. The activity will be present in the feed preparation, RA Column, and waste handling cells. Approximately 99% of the radioactivity will be removed with the RAW. For most maintenance work it will be necessary to remove equipment from the areas associated with the process steps preceding the RC Column because of the high degree of contamination present. The radiation intensity in areas and equipment associated with process steps subsequent to this point, although designed for remote handling and maintenance, may possibly be reduced to a point permitting personnel to work on the equipment in place under SWP (Special Work Permit) conditions.

The decontamination of process equipment resolves itself essentially to the problem of removal of radioactivity from stainless steel. The structural and supporting elements of the plant are fabricated almost solely from concrete and mild steel. These are extremely difficult, if not impossible, to decontaminate. Within the plant, all non-stainless steel elements have been protected with Amercoat 23, 33, or 55. These protective coatings show good resistance to process chemicals and prohibit wetting of the structural elements with contaminants. The use of protective coatings also permits the employment of chemical reagents for decontamination purposes which might otherwise attack the unprotected surfaces.

Decontamination of the surfaces of equipment and structural elements in the Uranium Recovery Plant will necessarily be performed on the basis of empirical procedures which result from knowledge obtained at Hanford Works in plant practice and laboratory studies, and from experience at Oak Ridge National Laboratory (O.R.N.L.) in semiworks and pilot plant studies. The usefulness and feasibility of decontamination has been demonstrated at these sites.

Previously developed decontamination techniques have satisfied specific conditions but will not necessarily constitute optimum procedures for the Uranium Recovery Plant. For example, nitric acid is a widely used reagent which could give unfavorable results under some circumstances because of its etching action on stainless steel. Similarly, many other reagents have been reported to be effective in the removal of radioactivity, but the effects of their repeated use on the surface being treated have not been established.

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2. Terminology

The procedure of decontamination has given rise to the use of certain special terms and concepts.

The term <u>decontamination</u> is used to designate the removal of radioactive chemical elements from solid surfaces.

<u>Contaminants</u> are the radioactive elements present on the solid surface.

<u>Mechanism of contamination</u> is the means whereby the radioactive elements are transferred to and fixed to the solid surface.

<u>Decontamination methods</u> are the means utilized to remove the radioactive elements. They may be generally classified as (a) physical -- total or partial removal of the contaminated surface; (b) chemical -- reaction with the radioactive elements or the larger mass of the associated non-radioactive materials to convert to a soluble or extractable condition; and (c) physico-chemical -- suspension by surface active agents.

B. APPLICATION TO URANIUM RECOVERY PLANT

1. Factors Influencing Decontamination

Because of the similarity in process and design characteristics between the Redox and Uranium Recovery Plant, the factors influencing decontamination of surfaces are essentially the same for both plants. These factors are discussed in the Redox Technical Manual, Chapter XXIII, HW-18700.

2. Provisions for Application of Decontamination Procedures

2.1 Protective coatings or sheathing

Structural elements in the plant have been protected with a chemically resistant coating such as Amercoat 23, 33, or 55. Thermally insulated equipment in the evaporator and concentrator cells has been sheathed in thin sheet stainless steel to protect the insulation from radioactive solutions. This type of construction will facilitate removal of the gross radioactivity by simple water flushing.

2.2 Materials of construction

Process equipment normally wetted by process solutions has been fabricated almost entirely of stainless steel. Some important but relatively small elements utilize Stellite and Teflon. All of these materials have exceptionally good resistance to chemical attack and are expected to be decontaminable.

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3. Design Features

   Process equipment design utilizes drainable and flushable surfaces for all components normally in contact with process solutions. The process equipment also incorporates labyrinth-type seals for centrifuge and agitator shafts which, in conjunction with the vent header system, effectively prevent major contamination of the exterior surfaces of the process system.

C. STAINLESS STEEL

   The process equipment components (tanks, lines, pumps, etc.) of the Uranium Recovery Plant are fabricated almost entirely from the 300 series of chrome-nickel stainless steels. The specific type employed has been chosen on the basis of corrosion resistance and the type of fabrication permissible.

   Decontamination of stainless steel is achieved by empirically developed procedures which involve no distinction between the several types of 300-series steels.

   This contamination of stainless steel can be placed in four categories: (a) alpha contaminants on internal surfaces, (b) alpha contaminants on external surfaces, (c) beta and/or gamma contaminants on internal surfaces, (d) beta and/or gamma contaminants on external surfaces. The procedures which may be employed for decontaminating stainless steels falling into the above categories are described in the Redox Technical Manual, Chapter XXIII, HW-18700.

D. OTHER MATERIALS OF CONSTRUCTION

1. Iron and Carbon Steel

   Iron and carbon steel have been employed for machine and structural elements (e.g., electric motors, jumper braces) which are not normally wetted by process solutions. As installed, these elements are protected by a chemically resistant coating, Amercoat 23, 33, or 55. Experience with decontamination of unprotected iron or steel has been generally unfavorable. The Redox Technical Manual, Chapter XXIII, HW-18700, discusses the problems involved in decontaminating unprotected iron and carbon steel. Complete removal of the contaminated piece, if possible, appears to be the most practical solution to the problem.

2. Concrete

   Concrete, in the absence of a protective surface coating, retains contaminants. Chemical or physico-chemical reagents have not been effective in removing either chemically fixed or physically adsorbed radioactivity. The Uranium Recovery Plant has been designed and constructed on the basis that concrete surfaces will always be protected by a chemically resistant coating (Amercoat 23 or 33 in the cells and pits in which

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only aqueous process solutions occur and Amercoat 55 in the cells which may be exposed to solvent solutions). In the event of contamination which penetrates through to the concrete base material, only two courses appear practical: (a) physical removal of the contaminated surface, or (b) shielding of contaminated concrete surfaces to permit necessary work in the immediate area of contamination.

3. Other Materials

Decontamination methods for glass, lucite, and wood are discussed in the Redox Technical Manual, Chapter XXIII, HW-18700.

E. PROTECTIVE COATINGS

The surfaces embraced by this classification are second in importance only to the stainless steels, since the other principal materials of construction for radioactive zones (concrete, iron, and mild steel) do not generally lend themselves to decontamination by treatment with chemicals. Therefore, to permit decontamination of these essential materials of construction, they must be protected with a surface film.

1. Requirements and Components of a Protective Coating

The Redox Technical Manual, Chapter XXIII, HW-18700, contains a description of the general requirements and the components of a protective coating.

2. Decontaminants

Since the protective films are the only barrier to essentially permanent contamination of the base materials, it is important to use a decontaminant which will inflict the minimum damage to the coating. Highly reactive materials such as nitric acid, chromic acid, or caustic soda should be used only as a last resort. The following agents, listed in order of preference, have been found to be effective in removing beta and gamma contamination from coated surfaces. The effectiveness of the decontaminants in removing alpha contamination is not known.

Agent	Composition
(a) Versene	5% Versene, 1% Triton, pH 8-9.
(b) Acidic solution	0.3 $\underline{M}$ citric acid, 0.1% Aerosol O.T., 0.5 $\underline{M}$ HCl.
(c) Neutral solution	2.5% trisodium citrate, 0.2% Aerosol O.T., pH 7.0±0.1.
(d) Water	
(e) Detergent solutions	

Agent

(f) KMnO$_4$-NaHSO$_3$. This requires direct manual application of a 1 to 2 per cent KMnO$_4$ solution for a five-minute period followed by scrubbing with a 10 per cent solution of NaHSO$_3$ and, finally, wiping or washing with water.

Table XXIII-1 shows the comparative effectiveness of the first four recommended decontaminating agents in removing a contaminating solution prepared by dissolving an O.R.N.L. slug "cooled" 3 years.

3. Uranium Recovery Plant Protective Coatings

The protective coatings employed in the Uranium Recovery Plant for application on steel and concrete surfaces are Amercoat No. 23 and 55, and, to a lesser extent, Amercoat No. 33. The Amercoats are manufactured by the Amercoat Division of the American Pipe and Construction Company.

Amercoat No. 23 is a three-component vinyl chloride base resin coating, consisting of a prime, body, and seal coat. Application over existing Amercoat No. 23 will be accomplished by applying one prime coat, two body coats, and two seal coats, except where the existing coating requires patching. In this case it is essential to build up all broken areas with the original number of coats. Amercoat No. 23 is not resistant to the process solvent (tributyl phosphate in a hydrocarbon diluent) and is specified for use in non-solvent areas only.

Amercoat No. 33 is a single-component finish applied with a minimum of three coats. The base resin is polyvinyl chloride. The finish has essentially the same chemical and abrasion resistance as Amercoat No. 23 but is not suitable for prolonged immersion in aqueous solutions. Amercoat No. 33 is used only in those areas which are subject to wetting only by splashing or which are accessible to operating personnel for immediate flushing.

Amercoat No. 55 is a three-component finish consisting of prime, body, and seal coats. The base resin is polyvinyl chloride. The coating is formulated so that it has better resistance to concentrated (60%) nitric acid than either Amercoat No. 23 or No. 33. In addition Amercoat No. 55 possesses resistance to the process solvent (hydrocarbon and tributyl phosphate) and is employed to coat concrete and mild steel in the zones subjected to solvent wetting.

4. Polyethylene and Strippable Coatings

Although polyethylene (sheet or flame sprayed) and strippable coatings will not be employed in the Uranium Recovery Plant, the advantages of these coatings render their use desirable in certain applications. The coatings are discussed in detail in the Redox Technical Manual, Chapter XXIII, HW-18700.

F. SKIN

Skin decontamination is especially important because of the danger of the entrance of contaminants into the body, either orally or through skin breaks.

The ease of skin decontamination varies considerably among individuals and is largely dependent on the original condition of the skin. In all cases where a rough outer layer of skin is present, decontamination is more difficult until this outer layer is removed and the skin surface is polished.

Methods for skin decontamination are discussed in the Redox Technical Manual, Chapter XXIII, HW-18700.

G. CLOTHING

In those areas within the separation plant where there is a hazard of personnel contamination with radioactive materials, all persons entering are required to wear coveralls, shoe covers or overshoes, caps, and gloves as a protection against contamination of skin and street clothing. In addition to these items, towels, socks, undergarments, and shoes are furnished where required. Laundering and monitoring of the plant issue items are discussed in detail in the Redox Technical Manual, Chapter XXIII, HW-18700.

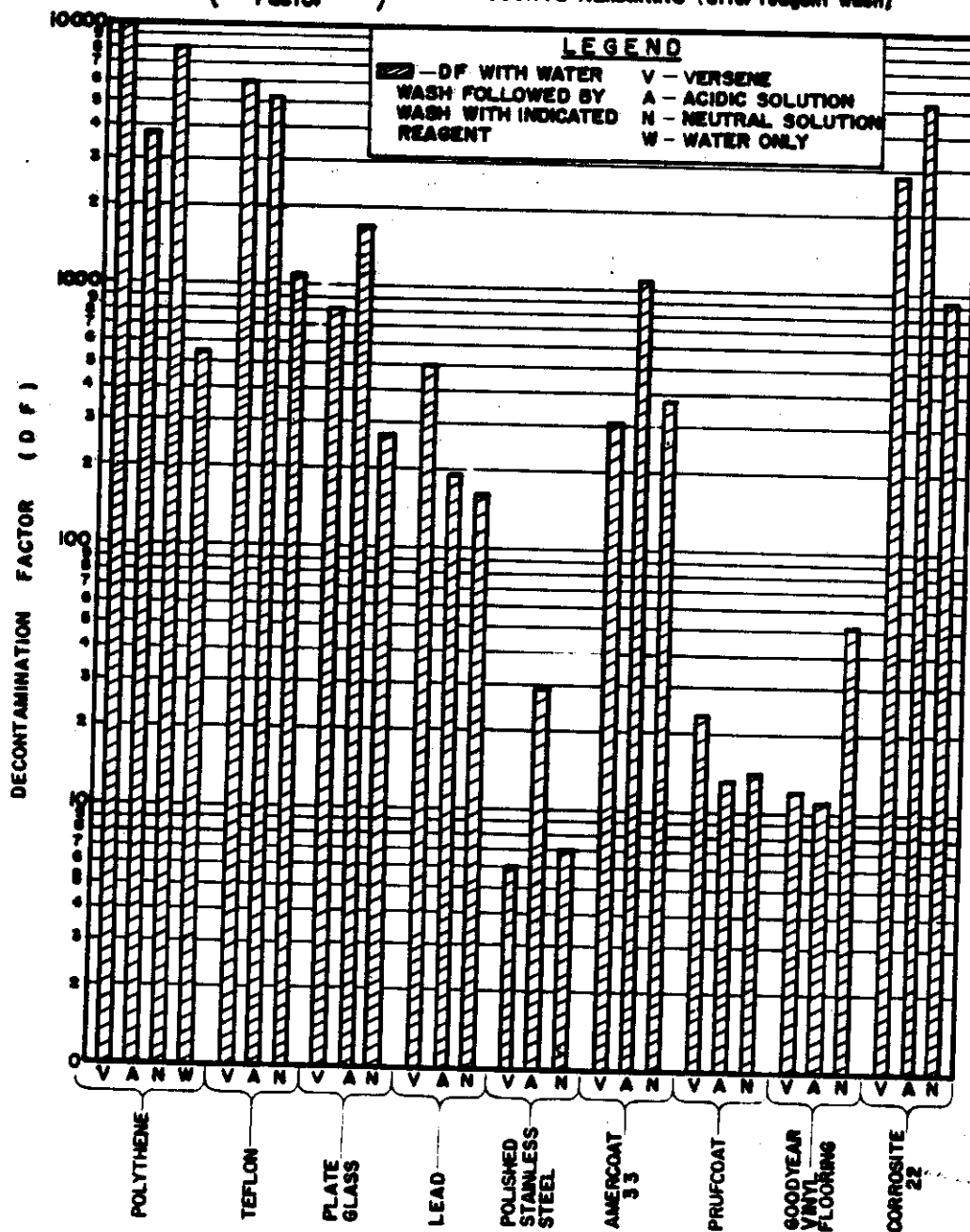## FIGURE XXII-1
DECONTAMINATION OF SELECTED MATERIALS WITH VARIOUS REAGENT WASHES
REFERENCE : ORNL 732

CONTAMINANT: FISSION PRODUCTS "COOLED" 3 YEARS
ACTIVITY APPLIED: 1.56 x 10⁶ COUNTS PER MINUTE GROSS BETA. SAMPLES SURVEYED BY MOUNTING ON A COUNTING CARD AND COUNTING WITH AN END WINDOW GEIGER-MULLER TUBE SUITABLY ARRANGED IN A LEAD PIG WITH A STANDARD SHELF TYPE HOLDER.

$$DF\left(\frac{Decontamination}{Factor}\right): \frac{BETA\ COUNTS\ APPLIED}{BETA\ COUNTS\ REMAINING\ (after\ reagent\ wash)}$$

LEGEND

-DF WITH WATER WASH FOLLOWED BY WASH WITH INDICATED REAGENT

V — VERSENE
A — ACIDIC SOLUTION
N — NEUTRAL SOLUTION
W — WATER ONLY

DECONTAMINATION FACTOR (D F)

POLYTHENE
TEFLON
PLATE GLASS
LEAD
POLISHED STAINLESS STEEL
AMERCOAT 33
PRUFCOAT
GOODYEAR VINYL FLOORING
CORROSITE 22

PART V: SAFETY, continued

CHAPTER XXIV. HAZARDS OTHER THAN RADIATION

CONTENTS

A. FLAMMABILITY AND EXPLOSIVENESS

The extensive use of an organic solvent in the TBP Plant introduces a potential hazard due to the flammability of the solvent. Safeguards against the possibility of a fire or explosion have been an important consideration in process and plant design. Careful selection of a solvent and proper design of equipment have resulted in a plant which may be operated safely.

The solvent (RAX) is a solution of tributyl phosphate (TBP) in a hydrocarbon diluent of the kerosene class. While both components are combustible, their relatively low volatilities and high flash points essentially preclude the possibility of fire or explosion under the conditions of their use. For instance, explosive mixtures of diluent vapor and air are not formed unless the diluent is heated well above normal cell temperatures; for TBP an even higher temperature is necessary. Those portions of the process which involve solvent are operated at low temperatures and are located in cells where no solutions are being heated. Vapors liberated by the solvent are contained within process vessels or discharged to the outside atmosphere by the ventilation system.

The nature and extent of the fire and explosion hazard, as well as the plant design features and operating practices to eliminate the hazard, are discussed in this chapter.

1. Physical Properties of Solvent (RAX)

1.1 Definitions

The relative hazard of a flammable liquid may be predicted from a knowledge of values for certain of its physical properties. The significant physical properties are defined below.

Flash point is the lowest temperature at which sufficient vapors are given off by a liquid to form flammable vapor-air mixtures capable of ignition by an open flame. Whereas other properties are factors in determining flammability of liquids, flash point is the principal indication of the hazard. Flash point determinations may be made in either closed-cup or open-cup apparatus. The results from the latter are affected by conditions of the room atmosphere and are usually several degrees higher than closed-cup flash points.

Lower explosive limit (L.E.L.) is the lowest percentage, by volume, of flammable vapor in air in which flame propagation can occur.

Upper explosive limit (U.E.L.) is the highest percentage, by volume, of flammable vapor in air in which flame propagation can occur.

Vapor-air mixtures outside the lower or upper explosive limits, respectively, are said to be too lean or too rich to support combustion. Flashes of flame will appear, but the flame will not propagate at an explosive rate.

Ignition temperature is the lowest temperature at which a flammable gas or vapor ignites spontaneously without the application of visible means of ignition.

Fire point is the lowest temperature at which a liquid will give off vapor sufficient for burning continuously when once ignited.

1.2 TBP

Tributyl phosphate, abbreviated TBP, is a colorless, odorless, organic liquid having a viscosity of 3.3 centipoises at room temperature, and a flash point similar to glycerine. It is used commercially as a plasticizer for lacquers. The properties of TBP relative to its flammability are as follows:

Vapor pressure (25°C.) -- approximately 0.002 mm.Hg [12]
(100°C.) -- approximately 0.25 mm.Hg
Flash point (closed-cup) -- 295°F. [12]

Due to the high flash point of TBP, no fire or explosion hazard arises from its use.

1.3 Diluent and solvent (RAX)

The diluent for TBP is a hydrocarbon liquid whose appearance and physical properties are those of a highly refined kerosene. Any one of several commercially produced solvents, possessing similar chemical and physical properties, may be used. A complete discussion of properties of typical diluents is included in Chapter IV.

In the refining of hydrocarbons of this type, low-boiling fractions, aromatic compounds, and unsaturated aliphatic compounds are removed. Deodorizing is accomplished by chemical treatment to remove sulfur compounds.

The properties of diluents relative to flammability are shown below. Except for fire points and flash points, values of these properties for specific diluents have not been published. In such cases values shown are for kerosene; however, they may be regarded as approximately correct for typical diluents.

Vapor pressure (25°C.) -- approximately 1 mm. Hg [9]
(100°C.) -- approximately 30 mm. Hg
Lower explosive limit -- 1.16% by volume [7]
Upper explosive limit -- 6.0% by volume [7]
Ignition temperature -- 490°F. [7]

Diluent	Flash Point, °F. Closed-Cup[11]	Open-Cup[13]	Fire Point,[13] °F.
Shell Spray Base	150	180	185
Deobase	162	185	195
Standard Oil Base Oil C	143	165	165

The addition of TBP to diluent lowers the diluent vapor pressure in proportion to the amount of TBP added. Vapor pressure lowering results in an increase in fire point and flash points. This effect is illustrated by a comparison of the data below[13] with those given above.

Solvent	Open-Cup Flash Point, °F.	Fire Point, °F.
Shell Spray Base + 12.5% TBP	155 (Closed-Cup)	195
Deobase + 12.5% TBP	200	200
Standard Oil Base Oil C + 12.5% TBP	185	185

As may be seen from the flash point data, explosive vapor-air mixtures are not formed unless the diluent (or solvent) is heated well above normal cell ambient temperatures.

2.   Location and Extent of Solvent Handling Hazard

The solvent handling facilities have been designed to minimize, insofar as possible, the hazards involved in the use of a flammable liquid. Those operations within the building which involve the use of solvent have been confined to five sections. The following vessels are used:

Name of Vessel	Vessel Number
RA Columns	ET 17-8 and ET 19-8
RC Columns	ET 17-2 and ET 19-2
RCW Receivers	TK 17-1 and TK 19-1
RO Columns	ET 18-2 and ET 20-2
ROO Receivers	TK 18-1 and TK 20-1
RAX Feed Tanks	TK 18-6 and TK 20-6
Organic Sump Holdup Tank	TK 5-1

Normally, the RAX Feed Tanks, TK 18-6 and TK 20-6, contain the bulk of the solvent. These tanks, having a working volume of 12,000 gal. each, are operated nearly full. The RCW Receivers, TK 17-1 and TK 19-1, of 1700 gal. capacity, and the ROO Receivers, TK 18-1 and TK 20-1, of 4500 gal. capacity each, "float" on the line. The normal hold-up volume in these tanks is approximately 20 per cent of the working volume. The remainder of the solvent is contained in columns and lines. Solvent which is collected in the Deep Cell, TK 5-6, may be recovered in the Organic Sump Holdup Tank, TK 5-1.

The fire and explosion hazard is not serious in these areas due to the high flash point and low volatility of the diluent. Flammable vapor-air mixtures are not produced unless the solvent is heated well above normal cell ambient temperatures. Heating of solvent tanks is not required in any portion of the process. Since tanks are closed to the cell atmosphere, vapors are confined, to a great extent, within the solvent tanks.

Solvent make-up and treatment facilities are provided in the 276-U Area, just outside the 221-U Building at Section 20. The following tanks are located in this area:

Name of Tank	Tank Number	Tank Volume, Gal.	Normal Tank Inventory, Gal.
Diluent Storage Tank	TK 380	25,000	20,000-25,000
TBP Storage Tank	TK 381	5,600	5,600
RAX Blend Tank	TK 382	16,000	0*
Organic Treatment Tank	TK 386	16,000	0*
Organic Receiver	TK 387	16,000	0*
Organic Treatment Sampler Tank	TK 388	2,400	0*

*) These tanks are used as required to reprocess off-standard solvent or to make up fresh solvent.

Diluent is received in tank-car quantities and is pumped to the Diluent Storage Tank, TK 380, where it is held for RAX make-up. Organic treatment, adjustments of TBP-diluent ratio, and similar operations are also performed in the 276-U Area. Heating of solvent is not contemplated; therefore, the formation of explosive mixtures is avoided. All tanks in this area are vented to the atmosphere.

Since the 276-U Area is an out-of-door installation, dilution of solvent vapors by the atmosphere provides an additional factor of safety.

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3. Plant Precautions

3.1 Electrical equipment

The National Electrical Code[10] has been followed in the installation of electrical equipment for the TBP process. Under this code, Class I locations are those locations in which flammable vapors are, or may be, present in sufficient quantities to form ignitable mixtures. Based on the method of handling, two divisions of Class I locations are established. Class I, Division 1, includes those locations where hazardous concentrations of flammable vapors exist continuously or frequently due to normal operating conditions or due to frequent maintenance and repair. Class I, Division 2, includes those locations in which flammable liquids are normally processed in closed systems, the location becoming hazardous only through equipment failure or abnormal operation. The TBP process is included in Class I, Division 2, since an abnormal operating condition, i.e., heating of the solvent, is necessary to produce explosive concentrations of solvent vapor.

Explosion-proof equipment is specified by the National Electrical Code for all Class I, Division 1, locations. In Class I, Division 2, locations, rigid conduit, flexible metal conduit, and ordinary electrical fittings and devices may be used. However, spark-producing devices such as switches, fuses, relays, and sliding motor contacts must be of an explosion-proof type or enclosed in an explosion-proof case. Since the 221-U Building is a Class I, Division 2, location, electrical installations are in accordance with that portion of the code.

3.2 Venting and ventilation

Organic handling vessels are vented either directly or through another vessel to the vessel vent header. A vacuum of 10 inches of water is maintained on the vessel vent header by a blower, which discharges into the ventilation tunnel. A slight negative pressure with respect to the cell is maintained in the vessels through the vessel vent header. Therefore, the tendency is for air to flow from the cell into the vessel, rather than for vessel vapors to escape into the cell. Normally, solvent vapors which are liberated within the vessel are continuously removed through the vessel vent header.

If solvent vapors should escape into the cells they will tend to collect at low points, since they are heavier than air. In this event the vapors are diluted with air and discharged to the atmosphere by the canyon ventilation system. Air, entering at the crane level, flows through the canyon into the cells. Vapors and air are exhausted from the cells through stainless steel headers located near the floor. These headers are connected through terra-cotta ducts to the ventilation tunnel and the 291-U Building. The ventilation system is described in more detail in Chapter XIII.

Inert-gas blanketing of process vessels is not necessary in the 221-U Building, due to the low volatility and high flash point of the solvent used. At normal operating temperatures the oxygen-diluent vapor ratio is well below the lower explosive limit. Solvent vapors are further diluted by ventilation and instrument air.

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4. Chemical Stability of Solvent

Laboratory tests at various A.E.C. sites have demonstrated the high degree of stability of the TBP-hydrocarbon diluent mixture in the presence of chemicals (including HNO_3 of all concentrations) used in the TBP process. In fact, this inertness toward HNO_3 plus the higher flash point of the TBP solvent represent the primary safety advantages of the TBP-hydrocarbon solvent over hexone, which is used in the Redox process.

However, because of the known reactivity of HNO_3 with olefins to form potentially hazardous dinitro-olefins (and to a lesser extent with aromatic hydrocarbons), the hydrocarbon diluent used in the TBP process should be essentially free of olefins and aromatics. To preclude the possibility of such nitrating reactions in the TBP Plant, diluent specifications conservatively permit a maximum olefin plus aromatic concentration of only 2 per cent. Although the maximum safe olefin concentration in the TBP solvent has not been demonstrated experimentally, diluent meeting the above specification (2 per cent olefins plus aromatics) is known to be well on the safe side.

B. PHYSIOLOGICAL EFFECTS OF PROCESS CHEMICALS

A review of the physiological effects of process chemicals is presented to assist supervision in recognizing and minimizing the potential health hazards in the TBP Plant. Maximum allowable concentrations (M.A.C.) are given for gaseous substances and those substances which may be present as mist or dust. The maximum allowable concentration is defined as the amount of a material to which the average worker may be exposed for 8 hours daily without significant harmful effects.

The chemicals and elements handled in the TBP process which may present a health hazard are TBP, hydrocarbon diluent, nitric acid, oxides of nitrogen, sodium hydroxide, uranium, plutonium, and fission products.

1. TBP (Tributyl Phosphate)

TBP is a colorless, odorless, organic liquid which resembles water in appearance. It has been used recently as a plasticizer for lacquers. Due to its low volatility, vapors are seldom present.

1.1 Tolerance concentrations

No limits are specified in the literature for either external exposure or ingestion.

1.2 Extent of hazard

Drums of TBP are received in carload lots at the 271-U unloading dock. The drums are emptied by a portable pump into the TBP Storage Tank, TK 381. The remainder of the TBP handling is done with permanently installed pumps and piping. Emptying of TBP drums involves a possibility of TBP contact with the skin. The hazard is also present during sampling solu-

1.3 Precautions

Equipment handling TBP was designed in accordance with normal chemical plant practice.

1.4 Physiological effects

No toxic effects due to TBP have been reported. However, the chemical has been used commercially only for a relatively short period. It is expected that TBP, like most organic solvents, will dissolve the oils of the skin, causing cracking and irritation.

2. Diluent

Hydrocarbon diluent used in the TBP process is a highly refined kerosene. The appearance and physical properties are very similar to those of commercial grades of kerosene. Diluent vapors, being heavier than air, tend to accumulate at low points.

2.1 Tolerance concentrations

No value for maximum allowable concentration for diluent or kerosene is quoted in the literature. Values for gasoline range from 200 p.p.m. to 1000 p.p.m., depending on the type of gasoline and the authority.[3][8] Since the irritant effects are generally more pronounced for higher boiling hydrocarbons, a maximum allowable concentration on the order of 500 p.p.m. appears to be justified. This is the figure quoted for Stoddard Solvent, a hydrocarbon distillate similar to the diluent used.[3]

2.2 Extent of hazard

Normally, the diluent inventory consists of 14,000 to 25,000 gallons in the canyon process vessels and up to 25,000 gallons in storage in the 276-U Solvent Handling Area. The possibility of contact of diluent with the skin during sampling operations or because of leaks or spills is probably the most likely potential hazard to be encountered in handling the diluent. Also, hazardous vapor concentrations are conceivable if large volumes of diluent were to be released to an operating area in some manner, such as by rupture of piping or process equipment.

2.3 Precautions

Equipment handling diluent was designed in accordance with normal chemical plant practice. In the 221-U Building, the ventilation system maintains diluent vapor concentrations at the canyon deck level well below the hazardous concentration, as previously discussed in this chapter (under A3.2). The 276-U Solvent Handling Area is an open area without walls or roof. Thus, any hazardous vapors present are allowed to escape to the surrounding atmosphere where they are diluted to negligibly low concentrations.

2.4 Physiological effects

Diluent is physiologically classed as an irritant. Inhalation of the vapor causes irritation of the mucous membrane of the eyes and nose. Watering of the eyes and coughing, with expectoration, are evidences of internal irritation.

In common with other organic solvents, diluent has the property of dissolving the oils of the skin, causing dryness, cracking of the skin, and irritation. Also, under unusual conditions, diluent may be an anesthetic hazard. The early symptoms are impairment of mental and physical facilities and dizziness. The probability of cumulative effects is slight where the vapor concentrations are not sufficient to cause dizziness.

It should be borne in mind that an atmosphere in which the solvent vapor concentration is below the explosive limit is not necessarily safe for breathing. The lower explosive limit for diluent (1.16%) corresponds to 11,600 p.p.m. (Cf. M.A.C. of 500 p.p.m.) If the symptoms of dizziness or irritation to the eyes and nose are experienced, the affected man should get fresh air immediately.

3. Nitric Acid

Nitric acid is a corrosive mineral acid which is widely used in the chemical industry. Contact with the skin produces severe burns. Therefore, the proper types of protective gloves, clothing, and goggles must be worn when handling this material.

3.1 Tolerance concentrations

No limits are specified in the literature for external surface exposure, but about 10 ml. (three fluid drams) of concentrated* nitric acid taken internally is considered a fatal dose.(2)

3.2 Extent of hazard

Daily process consumption of 60% nitric acid is 18,890 gallons, based on 10 tons per day uranium recovered. The bulk of this acid is used in slurry acidification and RAS preparation. Nitric acid used for organic treatment and decontamination is not included. The greatest contact hazards are experienced in decontamination and in sampling solutions containing nitric acid.

3.3 Precautions

As indicated above, the proper types of protective gloves, clothing, and goggles must be worn when handling nitric acid. Standard chemical plant design practice was followed in installation of the nitric acid handling facilities. Safety showers or hose bibs are provided at

*The exact concentration was not specified by the reference.

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strategic locations in operating areas to provide for rapid irrigation in cases of serious surface exposure.

3.4 Physiological effects

Indication of the magnitude of the contact hazard of nitric acid is given by tests which showed that 70% HNO_3 produces definite skin burns in 5 to 15 seconds. Burns of first, second, and third degree may result from nitric acid contact. Immediate irrigation of nitric acid splashes with water will greatly minimize its effect on the skin.

In case of ingestion, the patient should be given milk of magnesia, up to 8 fluid ounces, and quantities of water or milk, followed with egg whites and milk. Emetics and carbonates should be avoided.

4. Oxides of Nitrogen

Oxides of nitrogen are formed when nitric acid is spilled on organic or reducing materials such as sawdust or iron filings. These oxides, known generally as "nitrous fumes", consist of a mixture of NO, NO_2, and N_2O_4.

4.1 Tolerance concentrations

The effects of nitrous fumes over a wide concentration range are listed below:[5][6]

Concentration, as NO_2, in Parts per Million	Physiological Response
200 to 700	Rapidly fatal for short exposures. (1/2 hr. or less at 700 p.p.m.)
100 to 150	Dangerous for even a short period. (1/2 to 1 hr.)
100	Least amount causing coughing.
60	Least amount causing immediate throat irritation.
10	Maximum concentration (MAC) for continuous exposure according to Massachusetts state law, recognized by most authorities.

4.2 Extent of hazard

Under normal operating conditions nitrous fumes are not liberated in the TBP process. Nitric acid contact with organic materials or metals, due to spills or improper decontamination procedures, represents the most seri-

ous hazard involving fumes of nitric acid.

4.3 Precautions

Since exposure to nitrous fumes can result only from accidents or operating errors, plant personnel must be responsible for the prevention of such incidents. Should nitrous fumes be inadvertently liberated in the plant, the affected area should be cleared of personnel until the fumes have been removed by the ventilation system. If it is necessary for an individual to enter an area where nitrous fumes are present, he should be equipped with a suitable air mask and protective clothing.

The presence of oxides of nitrogen may be detected by odor and, to a certain extent, by color.[8] A characteristic odor is distinct at concentrations of less than 5 p.p.m. in air. In well-lighted areas, 100 p.p.m. or more of nitrogen dioxide (NO_2) in air exhibits a visible, reddish-brown tint. It should be noted, however, that other oxides of nitrogen (NO and N_2O_4) are practically colorless and that the relative proportions of the different molecular forms are temperature dependent. Thus, an atmosphere colored by oxides of nitrogen is probably dangerous, but the absence of color does not necessarily indicate safety.

The concentration of oxides of nitrogen in air can be determined precisely over the range of 5 to 500 p.p.m. by volume using the phenoldisulfonic acid method.[1]

4.4 Physiological effects

Inhalation of nitrous fumes in concentrations above 60 p.p.m. at first causes a painful burning and choking sensation. Exposure to concentrations greater than 120 p.p.m. may cause immediate loss of consciousness. In either case, the aftereffects of the exposure can be very serious, leading to pulmonary edema (swelling of the lung tissue due to effusion of a watery liquid into the cellular tissue) developing several hours after exposure. The greatest danger from nitrous fumes is from exposure to concentrations less than 60 p.p.m. Concentrations in this range do not cause any immediate discomfort, but can result in a delayed effect.[4]

Complete rest is very important after inhalation of nitrous fumes. The individual should be removed, or remove himself, from the nitrous fumes as soon as possible. It is most important that the exposed individual does not exert himself, and that he lie down to rest while waiting for transportation to the hospital. He should be kept warm.

5. Sodium Hydroxide

Sodium hydroxide is a chemical widely used in industry. Proper protective equipment, such as gloves, clothing, and goggles should be worn when handling sodium hydroxide.

5.1 Tolerance concentrations

No limits are specified in the literature for external exposure, but about 2 grams (30 grains) of NaOH taken internally may be sufficient to cause death.(2)

5.2 Extent of hazard

Based on uranium recovery of 10 tons per day, the daily process consumption of 50% NaOH is 7660 gallons (97,400 lb.). This entire amount is required for neutralization of the combined process wastes.

5.3 Precautions

Equipment handling sodium hydroxide solutions has been designed in accordance with normal chemical plant practice. As indicated above, the proper protective clothing should be worn by operating personnel.

5.4 Physiological effects

Sodium hydroxide is a dangerous alkali to handle, as either the dry chemical or its solutions quickly attack the flesh and eyes. Severe burns, dehydration of skin tissue, deep seated, slowly healing ulcers, and loss of fingernails may result from chemical reaction with sodium hydroxide. There appears to be an inactive period between the time of contact with caustic and the appearance of the actual burn. No time should be lost in washing the part with water, since the inactive period probably does not exceed a few minutes. The skin should be washed with 2% acetic acid, followed by water, to neutralize the residual caustic. If the caustic is splashed in the eyes, they should be washed with 5% boric acid solution.

Sodium hydroxide, when dispersed as a dust or mist of concentrated solutions, is intensly irritating to the upper respiratory organs. Ulceration of the nasal passages may result from long or severe exposure to such compounds. Swallowing caustic solutions is considered deadly. If sodium hydroxide has been swallowed, the patient should be given 2% acetic acid, up to 6 fluid ounces, followed by egg whites and milk. The patient should be kept quiet and warm.

6. Uranium, Plutonium, and Radioactive Fission Products

Uranium, plutonium, and radioactive fission products represent a serious health hazard. The principal physiological effects of these substances are due to their radioactivity. The hazards involved in their handling are discussed in Chapter XXI.

7. Other Process Chemicals

The other process chemicals, sulfamic acid, ferrous ammonium sulfate, sodium sulfate, and calcium carbonate, are not hazardous enough
led discussion. Reasonable care should be exercised,
ing them to avoid skin contact and insure that ingestion

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